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CYCLIC VOLTAMMETRY STUDY OF Ce(IV)/Ce(III) REDOX COUPLE AND Ce(IV)-F COMPLEX IN SULFURIC ACID MEDIUM

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In this paper the electrochemical behaviors of Ce(IV)/Ce(III) redox couple and Ce(IV) - F complex in sulfuric acid medium were studied by cyclic voltammetry using a platinum electrode. Both of the Ce(IV)/Ce(III) couple in Ce(IV) solution and Ce(IV) - F complex is a quasi-reversible process, and gives a linear correlation between the peak potentials and square root of scan rates, showing that the kinetics of the overall process is diffusion controlled. The complexation of cerium(IV) and fluoride is favorable for the oxidation of Ce(III). The kinetic parameters such as diffusion coefficients, anodic transfer coefficients and rate constants were studied.

Key word: cyclic voltammetry, Ce(IV)/Ce(III) couple, CeF_2^{2+} complex ion, oxidation

INTRODUCTION

Cerium is one of the most important rare earth elements due to its specific functional applications, which is widely used in industry and metallurgy as a material for ceramic, catalyst, polishing powder and sulfide controlling additive for steel and other alloys [1]. The traditional methods to extract cerium are solvent extraction or ion exchange method. But there are some shortcomings such as large investment, more steps and high cost. Compared with chemical method, the electrochemical method has the advantages of convenient measurement operation, simple equipment, accurate result, especially the continuous appearance of new ion-selective electrodes, making it widely used in rare earth hydrometallurgy [2].

Currently, the method of "electrolytic oxidation - extraction" has been applied in production of ceric oxide, which has the advantages of without introducing of chemical reagent, low production cost and high product purity. On the basis of this technology, the electrochemical study of cerium has important meaning.

Bastnaesite ($ReCO_3F$, Re = Rare earths) is the main abundance of cerium in minerals, which theoretically contains about 50 % cerium, 0,2 - 0,3 % thorium and 8 - 10 % fluorine, etc [3]. Recently, the main technology for bastnaesite treatment is "oxidizing roasting - sulfuric acid leaching - solvent extraction" [4]. However, the fluorine element will be leached out by sulfuric acid, and mainly exists in the form of $[CeF_2]^{2+}$ complex ions in the fluorine-bearing cerium sulfate solution, which makes it difficult to separate F^- and Ce^{4+} [5]. Up to now, the electrochemical of the Ce(IV)/Ce(III) redox couple in sulfuric acid has been widely investigated [6 - 9], however, there is no electrochemical study of Ce(IV) - F complex in sulfuric acid solution. In this paper, the electrochemical behaviors of Ce(IV)/Ce(III) and Ce(IV) - F complex in sulfuric acid solutions were investigated by cyclic voltammetry using a platinum electrode. The objective of this paper is to study the redox property of Ce(IV)/Ce(III) and Ce(IV) - F complex, and provide valuable data for the electrolytic oxidation of cerium in fluorine-bearing cerium sulfate solution.

ELECTROCHEMICAL MEASUREMENTS

All reagents of analytical grade were purchased from Shenyang Guoyao Group Chemical Reagent Co., Ltd.

The stock solutions of Ce(IV) and Ce(IV) - F were prepared by treating the sulfuric acid, sodium fluoride, and cerium (IV) sulfate in stoichiometric amounts to volumetric flask and then adding water to get the desired concentrations of the cerium and acid. All solutions were prepared using deionised water with resistivities > 18,23 MΩ/cm.

Cyclic voltammetry (CV) measurements were performed with a three-electrode system using an AUTOLAB PGSTAT30 (made in Netherland) connected with a personal computer. The working electrode was a platinum electrode with an area of 0,12 ± 0,004 cm^2. The counter electrode was a platinum wire electrode and the reference electrode was a saturated calomel electrode (SCE) electrode. Before experiment, the working electrode was first polished with a microcloth using alumina slurry and then rinsed with distilled water several times. Thereafter the electrochemically activity was confirmed by cyclic voltammograms in 0,1 mol/l H_2SO_4

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solution. All the experiments were performed at room temperature(25 ± 2 °C) in a 100 ml electrolytic cell.

RESULTS AND DISCUSSION

Cyclic voltammetric behavior of Ce(IV) / Ce(III) in sulfuric acid

The cyclic voltammograms for the Ce(IV) / Ce(III) in sulfuric acid medium are shown in Figure 1. In all experiments, a cathodic peak appeared at 0,4 V indicates the reduction of the platinum oxide. It is also shown that the anodic peak (E_{pa}) associated with the oxidation of Ce(III) to Ce(IV) occurs around 1,38V, and the cathodic peak (E_{pc}) associated with the reduction of Ce(IV) to Ce(III) occurs at approximately 1,07 V versus SCE. The anodic peak and cathodic peak potentials change gradually with the increase of scan rate from 20 to 300 mV/s. The formal equilibrium potential ($E^{o\prime}$) of the Ce(IV)/Ce(III) couple taken to be the average of the anodic peak and cathodic peak values is about 1,22, which is close to a reported value (1,19 V) using a glassy carbon disk electrode [8], and the separation of peak potentials (ΔE_p) is far more than 59 mV and increase with the increase of scan rate. The ratio of anodic peak current to cathodic peak current (I_{pa}/I_{pc}) is far from 1, suggesting that there are kinetic or other complications in the electrode process [10], and the complexation of Ce and SO_4^{2-} ions may be involved. As discussed above, the redox reaction of Ce(III)/Ce(IV) couple in sulfuric acid is an electrochemical quasi-reversible process.

From electrochemistry literatures [11, 12], the peak current obeys the Randles-Sevcik relationship, and is also a function of the difference between E_p and $E^{o\prime}$ at different scan rate, being related to the electron transfer coefficient and standard rate constant. The relationships can be described as following equations:

$$I_p = (2{,}69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2} \quad (1)$$

$$I_p = 0{,}227 nFAC k^0 \exp[-(\alpha nF/RT)](E_p - E^{o\prime}) \quad (2)$$

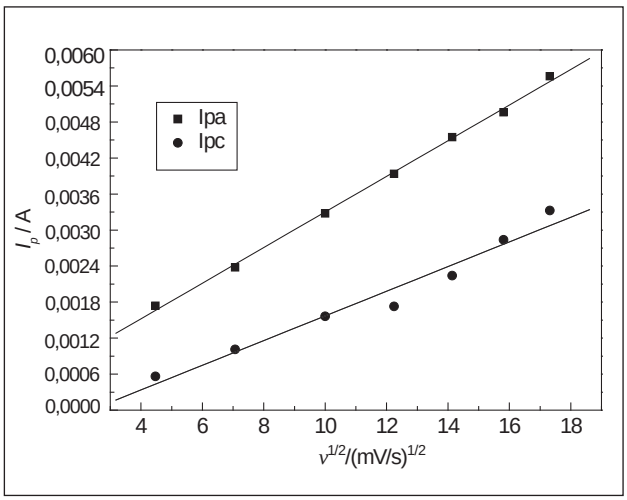

Figure 2 Plots of I_p vs. $v^{1/2}$

where n is the number of exchanged electrons, A is the electrode area, C is the solute concentration, D is the diffusion coefficient, v is the scan rate, F is faraday constant, R is universal gas constant, T is temperature, α is electron transfer coefficient and k^0 is standard rate constant.

The linear Randles-Sevcik relationship between peak currents and square root of scan rates is observed from Figure 2, indicating that the oxidation of Ce(III) and reduction of Ce(IV) are diffusion controlled. From the slopes of the plots, the anodic diffusion coefficient (D_a) is estimated to be $8{,}45 \times 10^{-5}$ cm^2/s and the cathodic diffusion coefficient (D_c) is $4{,}05 \times 10^{-5}$ cm^2/s. The difference in the diffusion coefficients reflects the difference in the state of complexation.

Figure 3 shows the plot of ln I_p vs. (E_p - $E^{o\prime}$), determined at different scan rates with a slope of - ($\alpha nF/RT$) and the intercept proportional to k^0. The anodic transfer coefficient (α_a) is calculated to be 0,16, which may be attributed to the large peak splitting. The rate constant (k^0) can be estimated to be $3{,}50 \times 10^{-3}$ cm/s.

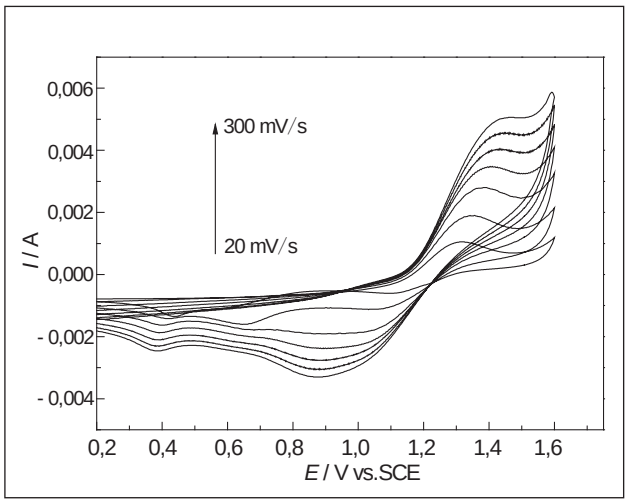

Figure 1 Cyclic voltammograms of Ce(IV) solution ($C_{Ce(IV)}$ = 0,1 mol/l, C_{H^+} = 1mol/l) at scan rates of 20, 50, 100, 150, 200, 250 and 300 mV/s

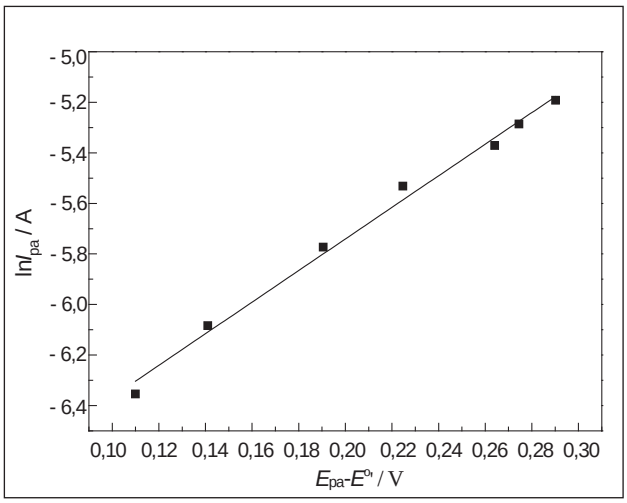

Figure 3 Plot of ln I_p vs. potential (E - $E^{o\prime}$)

Cyclic voltammetric behavior of Ce(IV) - F complex in sulfuric acid

It has been reported that cerium (IV) will complex with fluoride to form CeF_2^{2+} complex ions in sulfuric acid medium [5]. Figure 4 shows the cyclic voltammograms for the cerium (IV) - F complex solution in sulfuric acid medium. It is seen that the anodic and the cathodic peaks are around 1,28 V and 1,00 V, respectively. The formal equilibrium potential value is about 1,14, which is lower than that of Ce(IV)/Ce(III), and the peak currents significantly decrease with the adding of fluoride, indicating the occurrence of complex reaction between cerium(IV) and fluoride and the decrease of solution electrical conductivity. The anodic peak and cathodic peak potentials change slightly with the increase of scan rate from 50 to 300 mV/s, indicating that the peak potentials are dependent upon scan rate. The peak currents increase with the increase of scan rate and the separation of peak potentials is more than 59 mV. The ratio of anodic peak current to cathodic peak current is close to 1, showing a good reversibility of cerium (IV) - F complex. It also suggests that there are no other complications in the electrode process. These facts show that the electrochemical process is quasi-reversible, and the electrochemical reversibility is better than Ce(IV)/Ce(III) couple in sulfuric acid. The formal potential decreases and the oxidation peak potential shifts to a negative direction, indicating that the complexation of cerium(IV) and fluoride is favorable for the oxidation of Ce(III).

The cerium (IV) - F complex at various scan rates give a linear correlation between peak currents and square root of scan rates as shown in Figure 5, indicating that the kinetics of overall process are diffusion controlled. The anodic "line" and cathodic "line" are close and having similar slopes, the diffusion coefficients are calculated to be $3{,}04 \times 10^{-5}$ cm^2/s (D_a) and $3{,}10 \times 10^{-5}$ cm^2/s(D_c), respectively, which are much lower than that of Ce(IV)/Ce(III) couple in sulfuric acid. The similar diffusion coefficients also indicate the relatively comparable electron transfer rates. Figure 6 shows the plot of ln I_p vs. (E_p - $E^{o\prime}$). The anodic transfer coefficient (α_a) is calculated to be 0,25, and the rate constant (k^0) is estimated to be $2{,}32\times10^{-3}$ cm/s. According to the analyses above, the electrochemical reaction of cerium(IV) - F complex may be written as Eq.3.

$$CeF_2^{2+} - e \leftrightarrows CeF_2^{+} \quad (3)$$

Figure 7 shows the cyclic voltammograms of the cerium (IV)-F complex solution with various acidities. The anodic peak potential and current increase, while the cathodic peak potential and current decrease with the increase of acidity. The separation of peak potentials also increases with the increasing acidity. It shows that the increasing acidity goes against with the oxidation of Ce(III).

CONCLUSIONS

The electrochemical behaviors of Ce(IV)/Ce(III) redox couple and Ce(IV)-F complex ions in sulfuric acid medium were investigated by cyclic voltammetry using a platinum electrode. Both of the Ce(IV)/Ce(III) couple and Ce(IV) - F complex is quasi-reversible and diffusion controlled process. The electrochemical reversibility is more favorable when Ce(IV) complexed with fluoride. The complexation of cerium(IV) and fluoride is favorable for the oxidation of Ce(III), while the

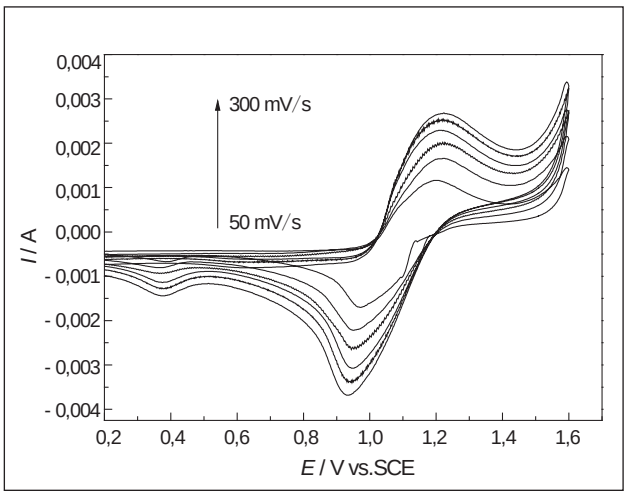

Figure 4 Cyclic voltammograms of Ce(IV)-F complex solution ($C_{Ce(IV)}$=0,1mol/l, n_F/n_{Ce}=2, C_H^+=1mol/l) at scan rates of 50, 100, 150, 200, 250 and 300 mV/s

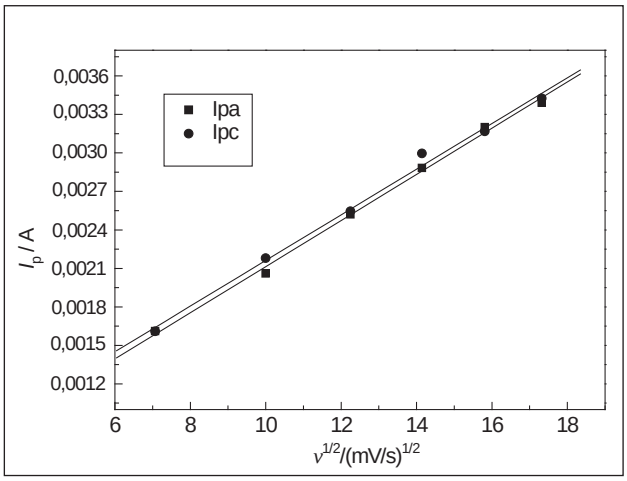

Figure 5 Plots of I_p vs. $v^{1/2}$

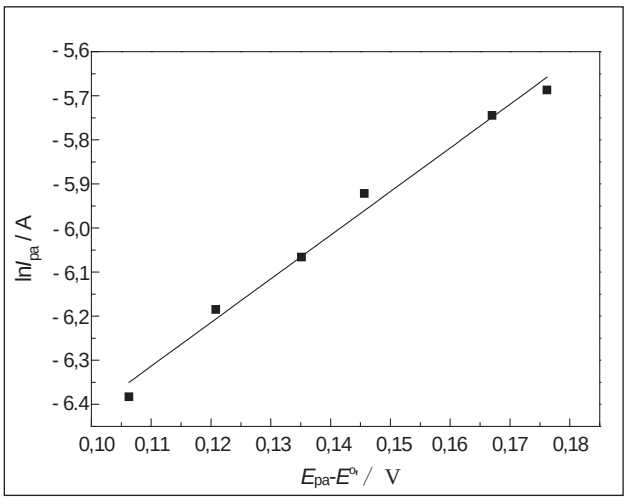

Figure 6 Plot of ln I_p vs. potential (E - $E^{o\prime}$)

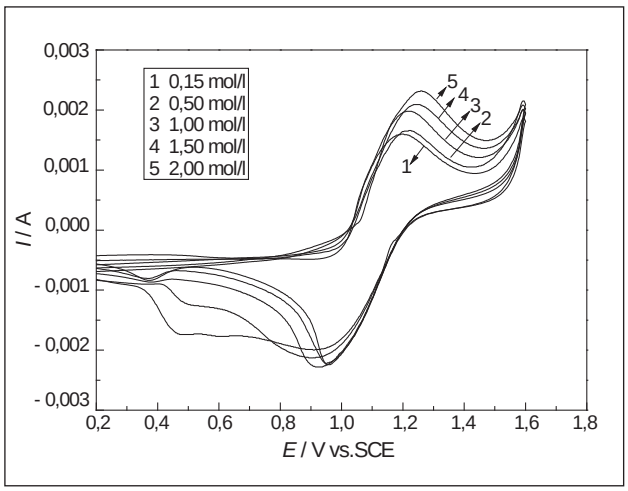

Figure 7 Cyclic voltammograms of Ce(IV - F complex solution with various acidities at a scan rate of 100 mV/s ($C_{Ce(IV)}$ = 0,1 mol/l, n_F/n_{Ce} = 2)

increasing acidity goes against with the oxidation of Ce(III). The diffusion coefficients, anodic transfer coefficients and the rate constants were determined.

Acknowledgements

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